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RAMAN SPECTRA OF THREE MONOSUBSTITUTED BENZENE COMPOUNDS IN THE SOLID STATE AT LOW TEMPERATURES*

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Plate XIII

ABSTRACT. The Raman spectra of $C_6H_5.COCH_3$, $C_6H_5.OC_2H_5$, and $C_6H_5.CHO$ in the liquid and in the solid state at different low temperatures have been investigated and the results have been compared with the available data on the ultraviolet absorption spectra of the substances obtained under similar conditions. Acetophenone produces four new lines at 34, 50, 83 and 94 cm^{-1} respectively in the solid state at - 90°C, while phenetole gives rise to a single new line at 96 cm^{-1} when the substance is solidified and cooled to - 90°C. With lowering of temperature to — 180°C, the low-frequency lines of acetophenone become sharper and the two lines at 83 and 94 cm^{-1} shift to 80 and 96 cm^{-1} respectively, while phenetole, under a similar change of temperature, gives rise to a second line at 83 cm^{-1}. Amongst the intramolecular lines, some of the lines due to C-H oscillations in both acetophenone and phenetole undergo some changes with change from liquid to solid phase.

Contrary to the case of the above two substances benzaldehyde does not produce any distinct line in the low frequency region when this compound is solidified, but instea dit gives rise to a feeble continuous wing extending upto about 100 cm^{-1} from the Rayleigh line.

Attempts have been made to interpret these results.

INTRODUCTION

The Raman spectra of a few monosubstituted benzene compounds in the solid state at low temperatures were studied by Ray (1950; 1951; 1952) and Biswas (1955). It was observed that the number, intensities and positions of the low-frequency lines are different for the different compounds, and they depend on the nature of the substituent group. Further, it was pointed out (Biswas, 1955) that in the case of methyl and ethyl benzoate the changes in the ultraviolet absorption spectra with change of state of these compounds furnish useful information regarding the appearance of low frequency lines in the Raman spectra of these substances in the solid state at low temperatures.

The compounds mentioned above have simple substituents excepting ethyl benzoate. The Raman spectra due to the solid phase of monosubstituted benzenes which have comparatively long and complicated substituent groups attached to the ring were not investigated by any previous worker. As the study

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of the Raman spectra of a few such monosubstituted benzenes in the solid state and a comparison of the results with the available data on their ultraviolet absorption spectra obtained under similar conditions might throw more light on the origin of these low-frequency lines, the Raman spectra of acetophenone, phenetole and benzaldehyde representing three different types of substituted benzenes have been studied in liquid and solid states and the results for two of these compounds have been compared with those for the ultraviolet absorption spectra studied under similar conditions by previous authors.

EXPERIMENTAL

The liquids acetophenone and benzaldehyde used in the present investigation were procured from E. Merck and phenetole was supplied by Fisher Scientitic & Co. U.S.A. They were distilled in vacuum as usual before being introduced in pyrex glass containers in which these substances were sealed and exposed to the incident radiation from a mercury arc. The technique and the experimental procedure for recording the Raman spectra of these substances in the solid state at different low temperatures were the same as described earlier (Biswas, 1954). The spectra were photographed on Ilford Zenith plates using a Fuess glass spectrograph of dispersion of about 11Å per mm. in the 4046Å region. On each spectrogram, iron arc spectrum was photographed for comparison.

RESULTS AND DISCUSSIONS

The Raman shifts observed for the three substances in the liquid and solid phase at different temperatures are given in Tables I–III. Some available data on the Raman spectra of these substances in the liquid phase as reported by earlier workers are also included in these tables. The low-frequency spectrum of acetophenone in the solid state at-90°C and –180°C respectively enlarged about four times are reproduced in figure 1, Plate XIII.

Acetophenone·

When this substance is solidified and cooled down to —90°C, four new lines at 34, 50, 83 and 94 cm^{-1} respectively appear in the low-frequency region. All these lines are quite intense and the two lines at 83 and 94 cm^{-1} are broad. When the temperature on the solidified mass is lowered to –180°C, the broad lines become sharper and the components of the pair at 83 and 94 cm^{-1} shift to 80 and 96 cm^{-1} respectively. In order to understand the origin of these lines in acetophenone, it would be interesting to compare the changes mentioned above with those observed in the ultraviolet absorption spectra of the substance by Deb (1951) with solidification of the liquid. He observed that when the substance is solidified and cooled down to —180°C, the absorption bands become much sharper and in place of the first broad band at 35744 cm^{-1} due to the liquid three sharper bands at 34170, 35249 and 36315 cm^{-1} respectively are recorded in the spectro-

gram due to the solid phase. Evidently, these three bands coalesce into one in the case of the liquid due to increase in the width of the individual bands. Moreover, the results given by the above author show that the ν_0-band as a whole shifts towards longer wavelength side by about 500 cm^{-1} with change from liquid to solid phase. Deb concluded that these changes on the absorption band with solidification are brought about as a result of intermolecular association amongst the molecules of the substance in its solid phase at low temperature.
Such association restricts the freedom of angular oscillation of the molecules about their axes and makes the bands sharper. The appearance of strong low-frequency lines in the Raman spectra due to solidified acetophenone both at $-90°C$ and $-180°C$ can be attributed to this phenomenon of intermolecular association in this substance. This case of acetophenone is very much similar to that of methyl benzoate described earlier (Biswas, 1955).

Amongst the Raman lines due to the single molecules of the substance the broad line at 162 cm^{-1} appears to shift to 166 cm^{-1} and the line at 1681 cm^{-1} to 1675 cm^{-1}. Moreover, the line at 3063 cm^{-1} due to C-H stretching oscillation appears to become stronger and the line 2920 cm^{-1} weaker when the substance is solidified and cooled to low temperatures. The two other lines at 2965 and 3007 cm^{-1} respectively due to C-H vibration seem to merge into one another to produce a line at 2998 cm^{-1} in the solid state. These changes may indicate that the association takes place mainly through these hydrogen bonds.

Phenetole:

When phenetole is solidified and cooled down to $-90°C$ a new Raman line appears at 96 cm^{-1}. When the temperature is further lowered to $-180°C$, this line shifts to 99 cm^{-1} and another comparatively weak line appears at 83 cm^{-1}. These results on the low-frequency spectrum of phenetole can be correlated with those on the ultraviolet absorption spectra of the substance obtained by Deb (1953) in the solid state at $-180°C$. He observed that the absorption bands of phenetole become sharper in the solid state at $-180°C$, but their positions are not appreciably altered with change from liquid to solid state. The diminution in the width of the bands is due to the restriction on the angular oscillations of the molecules which is brought about probably as a result of the formation of virtual linkages amongst the neighbouring molecules in the crystal lattice of the substance. The appearance of low-frequency Raman lines in solidified phenetole may be attributed to the oscillations of the molecules connected through these virtual bonds. In this particular case at $-90°C$, the molecules may not be linked to each other at more than one point, but at $-180°C$ new linkages may occur giving rise to the line 83 cm^{-1}. As the substituent group is rather large, the phenyl group is not surrounded by other phenyl groups in the lattice and therefore the virtual linkages formed at particular points of the molecule do not affect the excited electronic state of the molecule appreciably.

Fig. 1

Low frequency Raman spectrum of acetophenone

(a) Solid at − 180 C ; *(b)* Solid at about − 90 C

TABLE I

Acetophene

$\Delta\ \nu$ in cm^{-1}

Liquid		Solid (Present author)	
Murray *etal* (1942)	Present author	At about −90°C	At −180°C
	Continuous wing extending upto about 119cm^{-1}	34 (3)	34 (3)
		50 (3)	50 (4)
		83 (4b)	80 (3)
		94 (4b)	96 (5)
165 (5b)	162 (6b)	166 (4b)	166 (4b)
371 (3)	371 (2)	371 (1b)	371 (1b)
404 (0)	—	—	—
461 (0)	467 (0)	—	
588 (3)	589 (1)	—	—
617 (5)	617 (4)	617 (2)	617 (2)
732 (6)	728 (5)	731 (3)	731 (3)
767 (2)	755 (1)	—	—
852 (1)		—	
896 (0)	—	—	—
958 (3)	955 (2)	955 (0)	955 (0)
1002 (10)	999 (10)	999 (7)	999 (7)
1027 (6)	1023 (4)	1023 (3)	1023 (3)
1076 (6)	1077 (5)	1081 (3)	1081 (3)
1161 (4)	1154 (3)	1154 (1)	1154 (1)
1180 (3)	1181 (1)		
1267 (7)	1262 (5)	1262 (4)	1262 (4)
1301 (0)	—		—
1427 (1)	—		
1447 (1)	1443 (0)	—	—
1493 (3)	1491 (2)	1491 (0)	1491 (0)
1597 (10)	1595 (12)	1595 (8)	1595 (8)
1684 (10)	1681 (10)	1675 (7)	1675 (7)
2921 (6)	2920 (5)	2920 (1)	2920 (1)
2967 (2)	2965 (1)	2998 (2)	2998 (2)
3006 (2)	3007 (1)		
3065 (10)	3063 (6b)	3063 (7)	3063 (7)
3187 (1)			

TABLE II

Phenetole

$\Delta\ \nu$ in cm^{-1}

Liquid	Solid (Present author)	
	At about −90°C	At −180°C
Continuous wing extending upto about 114 cm^{-1}	96 (3)	83 (2) 99 (3)
177 (2)	177 (0)	177 (0)
241 (3b)	241 (0b)	245 (0b)
348 (5)	348 (2)	348 (3)
429 (3)	429 (1)	429 (2)
585 (1)	—	
614 (3)	614 (0)	614 (1)
762 (2)	--	762 (0)
799 (5)	799 (2)	799 (3)
923 (2)	923 (0)	923 (0)
998 (10)	998 (6)	998 (8)
1028 (5)	1028 (2)	1028 (3)
1117 (2)	1117 (1)	1117 (1)
1158 (3)	1158 (1)	1158 (2)
1245 (4)	1245 (2)	1245 (3)
1451 (1)	1451 (0)	1451 (0)
1490 (0)	-	-
1589 (4b)	1587 (2)	1587 (3)
1599 (6)	1599 (2)	1599 (3)
2884 (2)	2884 (1)	2884 (1)
2937 (6)	2932 (2)	2932 (3)
- -	—	2977 (1)
2986 (3)	2986 (1b)	2986 (1)
3065 (8b)	3063 (6) 3074 (7)	3063 (8) 3074 (9)

TABLE III

Benzaldehyde

$\Delta\ \nu$ in cm^{-1}

Liquid		Solid (Present author)	
Magat (1936)	Present author	At about −105°C	At −180°C
	Feeble wing extending upto about 95cm^{-1}	Feeble wing extending up to about 100cm^{-1}	Feeble wing extending upto about 100
137 (10b)	134 (4b)	134 (0b)	134 (0b)
234 (5b)	238 (3b)	238 (1b)	238 (1b)
439 (8)	435 (5)	435 (2)	435 (2)
613 (8)	605 (5)	605 (2)	605 (2)
646 (4)	652 (2)	652 (0)	652 (0)
745 (1)	747 (0)	—	—
827 (6)	826 (5)	826 (3)	826 (3)
—	850 (0)	—	—
1000 (15)	1000 (9)	1005 (6)	1005 (6)
1022 (4)	1020 (1)	1020 (0)	1020 (0)
1164 (12)	1167 (7)	1167 (4)	1167 (4)
1201 (12)	1200 (8)	1207 (5)	1207 (5)
1390 (3)	1389 (2)	1389 (0)	1389 (1)
1456 (3)	1459 (1)	1459 (0)	1459 (0)
1492 (3)	1490 (1)	1490 (0)	1490 (0)
1595 (15)	1594 (12)	1594 (8)	1594 (6)
—	1655 (2b)	1665 (1)	1665 (1)
1696 ± 13 (15b)	1701 (12b)	1701 (8b)	1701 (8b)
3060 (4)	3062 (7b)	3062 (5b)	3062 (5b)
Continuum 4358–4816 Å	—	—	—

With solidification of phenetole no other intramolecular oscillations except those due to the C-H oscillations undergo any appreciable change. In the case of the Raman lines due to C-H stretching oscillation however, the broad line due to the liquid at 3065 cm^{-1} is replaced in the solid state by two intense lines at 3063 and 3074 cm^{-1} respectively. Moreover, a comparatively weak line appears at 2977 cm^{-1} when the solid is cooled to −180°C. These changes in the Raman lines due to C-H oscillations indicate that these hydrogen atoms are mainly responsible for the intermolecular interaction in the solid state of this substance.

Benzaldehyde:

In the solid state at low temperatures, benzaldehyde does not exhibit any distinct Raman line in the low-frequency region, but a weak and continuous wing extending upto about 100 cm^{-1} on the longer wavelength side of the Rayleigh line appears to be superposed on the feeble wing which is present in the spectrum of the incident light. The wing accompanying the Rayleigh line due to the liquid is weak in comparison with such wing observed in other ordinary substituted benzene compounds. Thus it appears that when the wing due to the liquid is feeble, the new Raman lines of the low-frequency region are also very weak. The neighbouring molecules of benzaldehyde probably get associated in the liquid state through the OH virtual bonds and these associated groups being large, the wing due to the liquid phase is weaker. This happens because (1) the phenyl groups of adjacent molecules cannot come close together and (2) the associated groups being large the rotational freedom is restricted. It is presumed that the contribution to the intensity of the wing comes partly from oscillations in closely packed groups of the adjacent benzene rings in the liquid and also from the rotation of the single molecules.

Amongst the lines due to intramolecular oscillations the strong line at 1000 cm^{-1} due to the liquid phase shifts to 1005 cm^{-1} when the substance is solidified and cooled to low temperatures. It is observed from the data given by Magat (1936) that some previous authors have reported the existence of a continuous background in the visible region in the Raman spectrum of benzaldehyde in the liquid state. It is, however, observed in the present investigation that when the incident light is filtered through a dilute aqueous solution of $NaNO_2$, the continuous background in the visible region is completely absent. The presence of the continuum which was reported earlier may, therefore, be due to fluorescence excited in liquid benzaldehyde by the ultraviolet light of the incident beam.

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